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Soaking and freeze-drying of paper simulating water-damaged documents for salvage of archival materials.

Antonello A. Barresi; Antonio Capolongo; Giorgio Rovero - Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, corso Duca degli Abruzzi 24, 10129, Turin, Italy.

Introduction

The final goal of this work is to study the application of the freeze-drying process to water-damaged documents for restoration of archival materials. Water-damaging of paper material constituting archival and library documents can be due to different causes: direct ones, including floods, torrential rains, breaking of hydraulic or conditioning systems, and indirect ones, as consequence of fire extinguishment. In both cases, the main damages produced by water are absorption and swelling, cockling, adhesion of leaves, migration of inks and dyes, microbiological infection [1]. Alternatively to manual recovery, different drying methods as vacuum drying, freeze-drying and microwave drying were proposed [2-5]. Freeze-drying does not cause further damaging to water-soaked material, gives back an acceptable dried product and permits, through the freezing step, to stop all the degrading processes promoted by free liquid water, especially microbial attack and ink dissolution.

Although freeze-drying has been widely studied and applied in other fields as pharmaceutical and foodstuff industry, many open questions and problems remain, as the mathematical modelling of the drying kinetic. Unfortunately, in many cases there is not an appropriate dialogue between scientists, that do not know the restoring techniques and the connected problems, and the paper conservators that do not have the necessary knowledge of physics and engineering to produce the best process for a particular material. For this reason, the trial and error method is still widely utilised in this field.

Experimental and Results

As a first step it was necessary to set a reproducible method to prepare soaked samples simulating water-damaged paper material [6]. Since the present work has a preliminary character, the model system utilised was simpler than the real one. Modern blank paper 80 g/sheet, was utilised. Reams were cut to obtain sheets with dimensions of 4.2 cm × 5.9 cm; quality of freeze-dried paper was evaluated from a visual and tactical point of view [7]. Using modern blank paper rather than antique or costly material was advantageous for its low cost, physical-chemical reproducibility of the samples, and absence of dyes or inks that can be solubilized by water. Concerning the soaking step, distilled water was utilised in place of aqueous heterogeneous mixture containing mud or other solids.

The whole procedure for preparing reproducible soaked samples of paper consists of three successive steps: 1) conditioning of dry samples, 2) soaking and 3) drainage. The conditioning was carried out at 27 °C and relative humidity of 43.16 % for 48 hours [8]. A sample of conditioned dried paper was constituted by a block of 94 sheets that had a weigh of 18.08 ± 0.05 g (thickness 10 ± 1 mm) and residual moisture of 4.91 ± 0.04 %. Soaking of loosely blocked samples, maintained in vertical position, was carried out in distilled water at 27 °C. Soaking tests were carried out to determine an adequate soaking time in order to absorb the maximum amount of water; after 18 hours of soaking, the samples reached the saturation. A large dispersion in the experimental data was observed at shorter soaking times, that is probably due to inhomogeneous wetting of the paper sheets. Soaking for 18 hours and draining (at 27 °C and 100 % of relative humidity) for 5 hours, reproducible soaked samples were obtained; the amount of absorbed water was 121 ± 1 % with respect to the initial dry weigh.

Soaked samples were dried (pilot freeze-dryer Lyovac GT2, Leybold) through two different methods: "evaporating-drying" and freeze-drying. In the first case, soaked samples were placed on the cooling/heating plate at room temperature; the chamber pressure was then reduced to 32 Pa. In the second case, soaked samples were first frozen for 24 hours in a conventional freezer that permitted to reach a minimum product temperature of -20 °C and then transferred on the cooling/heating plate of the freeze-drier at room temperature; the chamber pressure was reduced to 32 Pa. During the freeze-drying processes, product temperature was monitored utilising thin unshielded Cu-costantane thermocouples placed on the top (under the first sheet) and in the middle of the samples; pressure was monitored by a Pirani gauge.

Soaked samples processed by freeze-drying and "evaporative-drying" were completely dried in 18 hours in both cases. The Figure shows the temperature profiles of the plate and the product. The temperature measurements confirmed that the product temperature is higher close to the surface than in the centre during the whole process because external ice sublimed before the internal one. In both cases the final quality of the dried samples was acceptable since only slight surface damaging was observed. This fact may be attributed to turbulent boiling of water that occurred during the initial period of both drying processes. During evaporative-drying this is obvious since liquid water is already present at the beginning of the process. On the contrary, during freeze-drying liquid water may be present as a consequence of ice thawing occurred transferring the samples from the freezer to the freeze-drier. To verify this hypothesis, soaked samples were frozen directly in the freeze-drier and then dried at 32 Pa. The samples were completely dried in 24 hours without surface damaging. These results suggested how to avoid the surface damaging of paper when freeze-drying pre-frozen or soaked material. In the first case may be convenient to set the freeze-drier plate at a temperature lower than 0 °C and to maintain this condition until all the liquid water is frozen (the time required depends on the mass of materials, the modality and time of the freeze-drier loading, etc.). In the second case it can be useful to cover the soaked documents with a sheet made of the same material or with a comparable porosity.

The secondary drying was studied separately from the primary drying on dry conditioned samples, at different values of pressure (85, 190 and 360 Pa). The results obtained showed that, in the range studied, pressure seemed to have no significant effect on the residual moisture of the samples. Unlike pharmaceuticals or foodstuff freeze-drying, secondary drying of paper is relatively short. In fact, after one hour the residual moisture was about 1 % whereas after three hours it was reduced to about 0.2 %. As a consequence of simultaneity of primary and secondary drying and the short duration of the latter, the results obtained suggested that it is difficult to stop the freeze-drying process in order to obtain completely dried paper having a 4 – 5 % of residual moisture. Referring to antique documents, especially those containing miniatures or paintings, conditioning of brittle dried paper is recommended before handling.

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Figure Temperature profiles of plate and product during a) drying with external freezing and b) "evaporating-drying". *h = 0*, thermocouple under the first sheet of paper; *h = 1/2*, thermocouple in the middle of the sample.